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CAUSE AND PREVENTION OF MICROFILM BLEMISHES

IN BRIEF ... NBS has studied the cause and prevention of microfilm blemishes. The study has shown that blemishes result from an oxidation-reduction reaction of the silver image by peroxides and other gaseous products evolved by the degradation of paper storage cartons. Results of the study have indicated measures for preventing microfilm blemishing.

A comprehensive study, by C. S. McCamy and C. I.

Pope of the NBS Institute for Basic Standards (U.S.

Department of Commerce), has revealed that gases evolved from paper and paper-lined storage cartons are responsible for the formation of blemishes on processed microfilm. Displacement of image silver has been pin-pointed to an oxidation-reduction reaction caused by peroxide and other gases. The blemishes have become known, therefore, as "redox blemishes." Fortunately, the study has also indicated that simple precautionary measures may be taken to eliminate redox blemishing.

McCamy, C.S., and Pope, C.I., Redox blemishes, their cause and prevention, presented at the National Microfilm Association Meeting held May 7, 1969, Boston, Mass.

Several years ago, there were reports of the formation of spots or blemishes on processed microfilm. As a great deal of information is stored on microfilm, this was cause for alarm among film manufacturers, archivists, Government agencies, and other records-keeping concerns. The extent of the concern is illustrated by the number of agencies that sponsored the research to solve the These were the National Archives and Records Service, the Library of Congress, the Social Security Administration, the Navy Bureau of Weapons, and the Adjutant General's Office of the Department of the Army. In addition, the National Microfilm Association solicited and secured financial support from the Bell and Howell Company, E. I. DuPont de Nemours and Company, Dynacolor Corporation, International Business Machines, Minnesota Mining and Manufacturing Company, Recordak Corporation, University Microfilms, and Xerox Corporation.

When it became apparent that blemish formation was a widespread problem, a field survey  $\frac{2}{}$  was conducted in which 100 trained inspectors examined over 7400 roles of microfilm in different Government agencies. More than 370 000 observations were recorded and then statistically analyzed at NBS. Among the findings of the survey were:

<sup>2/</sup> McCamy, C.S., Wiley, S.R., and Speckman, J.A., A survey of blemishes on processed microfilm, J. Res. Nat. Bur. Stand. (U.S.), 73A, 79 (1969).

blemishes existed in 6 different types; blemish formation was more severe in humid storage areas; films stored in metal containers were practically blemish free; films stored in air-conditioned areas were less prone to blemish; and, when there were no leaders on the film rolls, blemish formation was 2 to 3 times as severe as when film rolls had leaders of approximately 1.5 meters.

These factors tended to confirm the theory that products evolved from the paper storage cartons were responsible for blemish formation. Hydrogen peroxide is evolved as paper degrades and the rate of this reaction increases with the concentration of hydrogen peroxide. To simulate this natural storage condition in the laboratory, paper was immersed in a 5 percent hydrogen peroxide solution for thirty minutes, dried, and then sealed in jars with specimens of films at approximately 80 percent relative humidity. These films developed all the naturally occurring blemisnes within 30 days.

While this apparently confirmed the theory of peroxide induced blemish formation, other observations were
not explained. Studies elsewhere, 3/ for example, had
revealed that films fixed in solutions containing small
concentrations of iodide ions resisted blemish formation

<sup>3/</sup> Henn, R.E., Wiest, D.G., and Mack, B.D., Microscopic spots in processed microfilm: the effects of iodide, Phot. Sci. Eng. 9, 121 (1965).

in actual storage. Such films, however, did form blemishes in laboratory exposures to peroxide-treated paper. This suggested that factors other than peroxide were involved.

Further laboratory work was undertaken, which revealed that formaldehyde and formic acid were also evolved from the paper cartons. This work emphasized the fact that the susceptibility of films to blemish formation in the presence of peroxide is conditioned by other factors.

The silver grain, as formed in the gelatin matrix during development, is inherently unstable. In the normal photographic process, silver filaments become coated with sulfur atoms during fixation. It is this coating that stabilizes the grain structure. Films fixed a relatively long time and films retaining a small amount of hypo after washing acquire more sulfur and have been found to be quite resistant to blemish formation when they are exposed to peroxides, even at high humidity.

It was also found that when silver is oxidized and reduced in the presence of chloride ions, the reduced silver becomes incorporated with silver chloride in a colloidal form. Laboratory demonstrations have shown that a reddish colored colloidal silver is formed by the reaction of hydrogen peroxide with pure metallic silver in the presence of a small concentration of chloride ions. The characteristic color of the blemishes has been attributed to the presence of this colloidal material.

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This suggested an investigation into the effects of chlorine in the wash water on film stability. It was found that films washed in distilled water were faded by peroxide attack but typical blemishes did not form. A small concentration of chlorine, therefore, appears to be essential for formation of typical blemishes.

The study also revealed that the incidence of spots increased with the optical density of the image. In one experiment, a step tablet exposed to peroxide-treated paper developed blemishes on all steps having densities of 0.58 or more; none, however, formed at densities of 0.43 or less. The incidence of blemish formation also increased for each step above 0.58.

While the differences in blemishing on various brands of film were not significant, the processing equipment was found to be an important factor. In fact, the formation of blemishes on film processed by a particular machine so out-weighed the other statistics in the survey that it became necessary to run a second analysis without these data. Fortunately, this type of machine is no longer on the market.

Results of the study have indicated several precautionary measures that may be taken to prevent blemish formation:

- Use safety base permanent record film as specified in the ANSI (formerly USASI) specifications for photographic films for permanent records.
- 2. Use no higher densities than are required for the intended purposes and use dark characters on a light background if this is feasible.
- 3. Residual thiosulfate concentration should not exceed 1 microgram per square centimeter, but should be greater than zero. The optimum concentration appears to be about 0.5 microgram per square centimeter in a clear area.
- 4. Keep processing machinery and film clean.
- 5. Avoid scratching film.
- 6. Store films in containers made of inert materials, such as metals or plastics of proven quality. With good ventilation and clean air, the containers need not be sealed.
- 7. Do not permit storage temperature to exceed 70  $^{\circ}\mathrm{F}$  nor the relative humidity to exceed 40 percent.
- 8. Avoid wide-range cycling of temperature and humidity, since this accelerates the imbibition of gaseous contaminants.